

X-ray Fluorescence Spectroscopy Study of Coating Thickness and Base Metal Composition

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October 2008

Available from:

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LIST OF ACRONYMS

Al	aluminum
ASTM	American Society for Testing and Materials
Au	gold
Au/Cu	Au over Cu
Au/Ni/Cu	Au over Ni over Cu
Au/SS	Au over stainless steel
Cu	copper
EEE	electrical, electronic, and electromechanical
Ni	nickel
Ni/Cu	Ni over Cu
NIST	National Institute of Standards and Technology
SRM	standard reference materials
SS	stainless steel
μin	microinches
XRF	X-ray fluorescence

TECHNICAL MEMORANDUM

X-RAY FLUORESCENCE SPECTROSCOPY STUDY OF COATING THICKNESS AND BASE METAL COMPOSITION

1. INTRODUCTION

Nickel (Ni) and gold (Au) plated electrical, electronic, and electromechanical (EEE) parts are important components on many of NASA's missions. The thicknesses of these platings are significant. Even a small difference in measurements on the scale of microinches (μin) can alter the performance of a part. Completed parts must be analyzed to confirm that NASA standards were met in their manufacturing. Because of this crucial need for precision and economical solutions, a method that is fast, reliable, and preferably nondestructive has to be employed to ensure proper plating thickness.

A machine that is designed for this purpose is the x-ray fluorescence (XRF) spectrometer. This machine is practical in many different applications because it is able to measure bulk items in liquid, solid, and powdery forms with little or no preparation. It employs a nondestructive method that measures layer thickness and layer composition. The machine can also take measurements of substrate materials under several coatings.

As with any machine that performs measurements, great care must be taken to understand uncertainty in the data. Factors such as detection limitations of the machine or improper use of the machine can skew data. Without reliable data, parts that do not meet safety standards can be approved for use, introducing potential complications. The limitations on the data produced can be understood by comparing standards data to real parts data and subsequently applying statistical methods. By understanding the limitations in the collection of the data, accurate composition and thickness measurements can be obtained for samples with Au and Ni coatings.

2. BACKGROUND ON EQUIPMENT

Each XRF spectrometer varies in some aspect. Therefore, understanding the way a particular machine works is important to interpreting the data found. For this report, all data was acquired with a FischerScope® X-ray X-dal® machine, as shown in figure 1. The process starts with primary x-rays produced from an x-ray tube. When the primary x-rays strike the sample, the atom absorbs them. As the atoms in the sample absorb the x-rays, all of the energy is transferred to an electron. This energy removes it from the atom and leaves the atom in an unstable state. To return to a stable condition, electrons from the outer shell fall to the inner shell and subsequently give off characteristic x-rays, called XRF. A radiation detector then measures this secondary radiation. By sorting the energies of the x-rays received by the detector, the machine produces a spectrum of the XRF radiation. The sample's coating/substrate material combination is obtained from this spectrum. The intensity of each characteristic radiation is directly related to the amount of each element in the material.¹ Based on proprietary fundamental parameter methods, the Fischer software can compute the thickness and composition of the coating. Figures 2 and 3 are examples of XRF outputs.



Figure 1. FischerScope X-ray X-dal machine <<http://www.helmut-fischer.com>>.


FischerScope® XRAY XDAL		
		
NASA/MSFC ES43 EEE Parts Analysis Laboratory		
Product: 19 / Au/Ni/Cu		
Block: 217		
Application: 22 / Au/Ni/Cu		
Measuring time 20 sec		
Date: 6/26/2008 Time: 9:46:37 AM		
n= 1 Au 1 = 44.2 μ " Ni 2 = 24.0 μ "		
n= 2 Au 1 = 45.2 μ " Ni 2 = 17.2 μ "		
n= 3 Au 1 = 45.6 μ " Ni 2 = 17.4 μ "		
n= 4 Au 1 = 45.0 μ " Ni 2 = 18.6 μ "		
n= 5 Au 1 = 44.8 μ " Ni 2 = 18.7 μ "		
Element	Au 1	Ni 2
Mean	44.97	19.17
Standard deviation	0.511	2.764
C.O.V. (%)	1.14	14.42
Range	1.35 μ "	6.76 μ "
Number of readings	5	5
Min. reading	44.2 μ "	17.2 μ "
Max. reading	45.6 μ "	24.0 μ "

Figure 2. Sample report produced by XRF software.

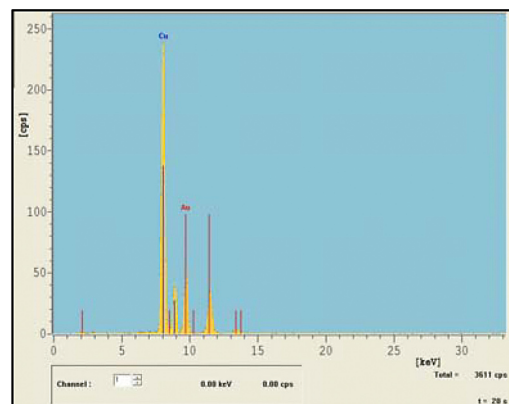


Figure 3. Energy spectrum produced by XRF.

In XRF spectrometry, consideration should be given to restricting the radiation to the area of interest by collimation at the radiation source. Collimators are thin translucent materials in different dimensions and shapes that narrow the beam of primary x-rays. This results in a reproducible, controlled, and well-defined primary x-ray beam geometry,¹ which increases the accuracy of measurements. The X-dal system is equipped with four collimators. The spherical collimators have diameters of 0.1, 0.3, and 0.6 mm. The rectangular collimator has dimensions of 0.15×0.5 mm. Another useful component of the FischerScope X-ray X-dal is a primary filter. The primary filter is used to influence the composition of the primary x-ray radiation so undesirable characteristics of the fluorescence spectrum, such as lower energy x-rays and scattered x-rays, can be avoided.

3. PROCEDURE

To understand the limitations of data found, measurements were taken as the parameters were varied and compared to true values of standard reference materials (SRM). Figure 4 shows SRM samples. The SRMs used were National Institute of Standards and Technology (NIST) traceable. Their thicknesses are certified to be within 5 percent of the true thicknesses. For every sample, six different parameters were varied to try to reduce measurement error: coating/substrate combination, number of layers, counting interval, collimator size, coating thickness, and test area location. Each measurement was taken five times in accordance with American Society for Testing and Materials (ASTM) International Standards,² which calls for the average of the five measurements to differ from the certified thickness by less than 10 percent at a 95 percent confidence level. The thicknesses of the samples used were chosen to fit in the range of 9.84–295 μin , the typical range of coating thicknesses used by EEE parts manufacturers. Staying in this range of thicknesses and using filters when appropriate ensured little or no error from poor secondary x-ray signal intensity. In this study, the main focus was on Ni and Au platings and their affect on different substrate compositions. Four different combinations were used as samples: Au over stainless steel (Au/SS), Au over copper (Au/Cu), Au over Ni over Cu (Au/Ni/Cu), and Ni over Cu (Ni/Cu).



Figure 4. Ni, Au, and Cu standards used as samples.

The standard states, “Measuring methods permit the simultaneous measurement of coating systems with up to three layers.”² Such measurements require unique data processing to separate the various characteristic emissions involved to allow for any secondary excitation that may occur between layers and to account for the absorption by intermediate layers. Two-layer and three-layer samples were used to try and further understand how to handle this limitation and any error resulting from testing multiple layers. The standard also states that counting intervals must be chosen in order to have a net count of at least 10,000 to reduce statistical error.² Samples were measured in different counting intervals to test for error in data due to insufficient count time.

By gathering data taken with different collimators, optimal collimator shapes can be found for specific samples. Four collimator sizes were tested. In addition to coating thickness, the composition of the substrate layer was measured. Measurements taken with a single coating, two coatings, and no coatings were compared to evaluate the impact that coating thickness had on the composition measurements of the substrate layer. Varying the areas tested and comparing their values is the best method to check the uniformity of coatings on parts. To simulate this, measurements were taken in fixed and randomized test areas to determine differences and similarities in error. All data were collected using a voltage of 50 kV to produce the primary x-ray.

4. DATA AND ANALYSIS

4.1 Two-Layered Samples With Gold Coatings

The first combination of coating/substrate measured was Au/SS. The SS used as a substrate was 302 (SS302). Four different coating thicknesses were used: 9.36, 46, 76, and 118 μin . The primary filter used was a Ni filter. The measurements included thicknesses of the coatings and the composition of the substrate layers. Although all the thicknesses found were all within 10 percent of the actual value, there were some problems with the composition measurements.

As coating thicknesses increased, so did the inaccuracy of the substrate composition measurements. In general, the percent composition of Ni was higher than expected, while the percent composition of chromium was much lower than expected. The composition of manganese was also inaccurate. In many instances, the measurements of substrate composition had an error of more than 10 percent. As the thickness approached 118 μin , the error approached 100 percent. Because of this large error in composition, more variables needed to be tested to find a way to reduce error. Since the Ni composition was the one with the most error overall, the first thing tested was changing the primary filter used.

Tests were run on the 46 μin Au/SS sample to determine if changing the primary filter or if extending the counting intervals would yield more accurate results. Figure 5 is a description of an Au/SS test run. To determine accuracy, the error was found with respect to the SS composition taken with no coating. No pattern in the percent error was observed as the primary filters were changed or as the counting intervals were changed. A calibration set was created and applied because changing these two parameters could not reduce the error.

Given that error of the measurements increased with Au thickness, the 118 μin sample was tested with a calibration set to reduce error. The composition percentages used in the calibration set for each element was the mean of all its composition measurements. When a calibration set was applied, the error in the thickness and composition measurements significantly dropped. Before a calibration set was applied, the thickness measurements were all under 10 percent; but the error dropped to below 5 percent with the calibration set applied. The composition measurements still had errors above 10 percent. Errors in the chromium and manganese measurements were often less than half of their original percentages when a calibration set was applied. From these tests, it was concluded that a calibration set could help reduce error dramatically when measuring substrate composition. The thicker the sample is, the less likely it will be to find accurate compositions for certain elements.

To see if the measurement of Au thickness would be influenced by the substrate composition, tests were performed on Au/Cu for 9.36, 46, 76, and 118 μin coatings, using a Ni primary filter. Notes for an Au/Cu test run are shown in figure 6. These tests measured the thickness of the Au coating. All the tests yielded favorable results with all measurements having errors under 10 percent.

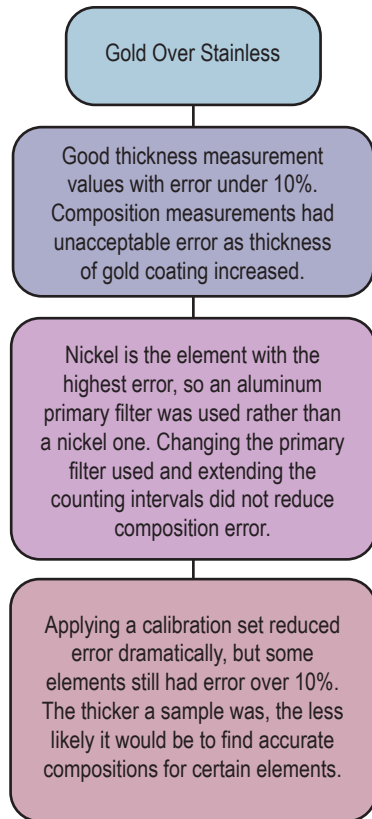


Figure 5. Description of Au/SS test run.

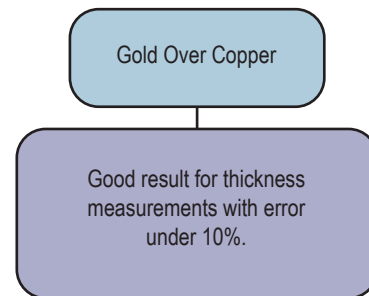


Figure 6. Notes for Au/Cu test run.

Errors were often under 5 percent except in the case of the thinnest sample. There was no clear pattern in the difference of percent error in thickness measurements between Au/Cu and Au/SS302, so case substrate composition did not affect the measurement of the coating thickness in this case.

4.2 Two-Layered Samples With Nickel Coatings

Measurements were taken of Ni/SS using SS302. Notes for the Ni/SS test run are shown in figure 7. The primary filter used was a Ni filter. The data collected were the thickness of the coating and the composition of the substrate layer. Both the thickness and composition measurements had unacceptable error. The thickness measurements had higher than 50-percent error. The results for the composition were also poor. The Ni percentages were in the negative range and the iron percentages were higher than expected. Because of such high percentages of error in the data, it was concluded that samples with Ni layers must be tested with an aluminum (Al) primary filter.

To test how an Al primary filter would affect the data obtained from samples with Ni layers, measurements of the coating thicknesses were taken of Ni/Cu. The thicknesses of the samples used were 4.24, 19, 49, 79, and 96 μm . The samples tested that had measurements with an error of more than 10 percent were the 4.24 and 19 μm coatings. The 19 μm coating had an error of more than 10 percent with the first collimator for a 10-sec time interval with varied test areas. A test was run

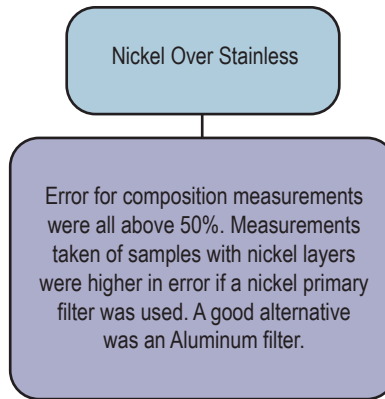


Figure 7. Notes for Ni/SS test run.

again under these conditions and the error found was 1.05 percent, a large decrease from the original error of 12.1 percent. Therefore, it was concluded that the large error was due to an operator error.

With the 4.24 μin sample, almost all the test runs had errors above 10 percent. The first thing that was tested to try and eliminate this error was increasing the counting interval. All of the original tests were repeated with a 60-sec interval run. An example of a repeated 60-sec interval run is shown in figure 8. The resulting values of the error in the measurements were significantly lower than the original numbers. These results suggest that a longer counting interval is needed when measuring thin samples.

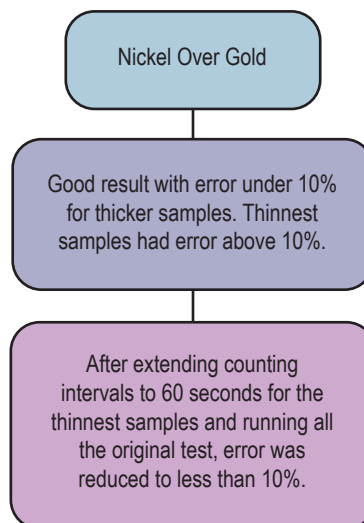


Figure 8. An example of a repeated 60-sec interval run.

4.3 Three-Layered Samples

The three-layered sample tested in this study was Au/Ni/Cu. The thicknesses of the Au samples used were 46, 76, and 118 μm and the thicknesses of the Ni samples used were 19, 49, 79, and 96 μm . To better understand how the accuracy of the measurements changed with the different primary filters, tests were done on the 46- μm Au over the 39- μm Ni over the Cu. Each collimator was tested for 20 sec on a fixed test area. Measurements were taken of the Au and Ni layers and their error was compared. The Al filters generated more accurate results, so the remaining tests were done with an Al filter. Figure 9 is a description of an investigation regarding accuracies obtained using either Ni or Al filters for a three-layer sample.

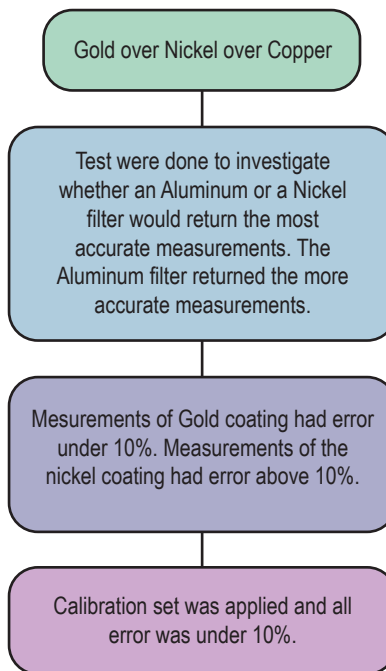


Figure 9. Description of investigation regarding accuracies obtained using either Ni or Al filters for a three-layer sample.

As the Au thicknesses of the samples were increased, the error of the Ni thickness measurements increased above 10 percent. The error for the Ni thickness with an Au coating was much higher than the error of the measurements found for Ni samples with no coating. In addition, the frequency of the first collimator not being able to obtain measurements of Ni thickness increased with the increasing Ni thickness.

As the thickness of the Au coating was increased, the error in the Au thickness measurements decreased. In addition, as the thickness of the Au increased, the error of the measurements of the Au thickness in the three-layered sample became less than the error of the measurements of the Au/Cu sample. Because of the large error in measurements, a calibration set was applied to reduce the error. When a calibration set was applied, the error was smaller than 10 percent, often less than the error in the measurements taken for the two-layered samples.

5. CONCLUSIONS

To summarize, the XRF spectrometer is an excellent machine for checking that EEE parts meet the standards. Obtaining accurate coating thickness and substrate composition measurements is possible if consideration is taken. When dealing with thinner samples, it is often beneficial to use longer counting intervals to reduce error. As the thicknesses of the samples were increased, the error also increased. Thick coatings become a problem when trying to obtain substrate composition. In this instance, a calibration set is useful in reducing the error. Thicker coatings resulted in inaccurate measurements even with the use of a calibration set; this error was reduced as thickness of the coating was reduced. Reducing error is more difficult when analyzing three-layered samples. Calibration sets need to be applied to obtain measurements with acceptable error per the ASTM standard.

When using the smallest collimator, 10- and 20-sec time intervals did not produce more than 10,000 counts. The low amount of counts sometimes resulted in increased error. Increasing the time interval can reduce the error of the measurements taken by the first collimator. A common pattern in the amount of counts was an increase in counts per sec with an increase of collimator size. As the collimator size is decreased, there is also a decrease in the intensity of the signals read by the detector. This can also lead to increased error. Simply increasing the collimator size cannot reduce error because other factors affect the accuracy. As the size increases, the detector receives more signals that often include background noise, which can lead to an increase in error. When dealing with three-layered samples, the smaller collimators can be used to reduce error from interfering signals. Because so many factors affect what collimator will be the most accurate for each sample, a general relationship between collimator size and error cannot be found.

These tests also compared the error of measurements taken in fixed or randomized test areas. No significant differences were found between the errors in the fixed and random test area measurements. These measurements often had small standard deviations, even though they increased when an Al filter was used rather than a Ni filter.

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operation and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE October 2008	3. REPORT TYPE AND DATES COVERED Technical Memorandum		
4. TITLE AND SUBTITLE X-ray Fluorescence Spectroscopy Study of Coating Thickness and Base Metal Composition		5. FUNDING NUMBERS		
6. AUTHORS T.D. Rolin and Y. Leszczuk*				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) George C. Marshall Space Flight Center Marshall Space Flight Center, AL 35812 * University of Michigan, Material Science Department, Ann Arbor, MI 48109		8. PERFORMING ORGANIZATION REPORT NUMBER M-1243		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA/TM-2008-215578		
11. SUPPLEMENTARY NOTES Prepared by Space Systems Department				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified-Unlimited Subject Category 38 Availability: NASA CASI 443-757-5802		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) For electrical, electronic, and electromechanical (EEE) parts to be approved for space use, they must be able to meet safety standards approved by NASA. A fast, reliable, and precise method is needed to make sure these standards are met. Many EEE parts are coated in gold (Au) and nickel (Ni), and the thickness coating is crucial to a part's performance. A nondestructive method that is efficient in measuring coating thickness is x-ray fluorescence (XRF) spectroscopy. The XRF spectrometer is a machine designed to measure layer thickness and composition of single or multilayered samples. By understanding the limitations in the collection of the data by this method, accurate composition and thickness measurements can be obtained for samples with Au and Ni coatings. To understand the limitations of data found, measurements were taken with the XRF spectrometer and compared to true values of standard reference materials (SRM) that were National Institute of Standards and Technology (NIST) traceable. For every sample, six different parameters were varied to understand measurement error: coating/substrate combination, number of layers, counting interval, collimator size, coating thickness, and test area location. Each measurement was taken in accordance with standards set by the American Society for Testing and Materials (ASTM) International Standard B 568.				
14. SUBJECT TERMS X-ray, fluorescence spectroscopy, measurement, coating thickness, elemental composition		15. NUMBER OF PAGES 20		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

National Aeronautics and
Space Administration
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